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Coin-size coiled-up polymer foil thermoelectric power generator for wearable electronics

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Abstract

A coiled-up thermoelectric micro power generator is presented using metal films sputtered on a thin polyimide foil. The principle of coiling-up yields higher voltages at a smaller generator area. Design optimizations were made for maximum long-term power output using the human body as heat source. It is shown that for low-power electronics like a wrist-watch even simple materials are sufficient and allow lowest-cost production, e.g. screen printing. Thermoelectrical screen-printing pastes were developed and results of first screen printed thermocouples are given.

Keywords: Thermoelectric power generator; Polymer foil; Screen-printing

1. Introduction

Wearable electronic normally run with batteries. This method of energy supply has some severe disadvantages that cannot be neglected: as everybody knows, batteries do not last forever and have to be renewed after some time, at least after a few years. Furthermore they contain chemical substances that can harm the environment. So its worth looking for alternative power supplies—especially for devices with very small energy consumption. A wrist-watch or a hearing aid for example only need power in the μW-range.

The most common alternative is the solar cell. Solar-driven watches are commercially available since decades. But since the normally used silicon-based cells are more expensive compared to a common battery, only few customers buy these watches.

Besides solar-cells, thermoelectric power generators provide another environment-friendly solution.

Here heat energy is converted into electric current using the temperature difference between a heat source and a heat sink. There are thermoelectric generators, fabricated by means of thin film techniques using Bi_2Te_3-thermocouples on silicon substrates [1,2]. In order to minimize heat-loss through the substrate the silicon even can be thinned to a small membrane [3]. Also thermoelectric power generators with flexible polymer foil substrates are known. Qu et al. [4] present a generator where electroplated thermocouples of antimony and bismuth are embedded in a 50 μm thick flexible epoxy film, and Stordeur [5] fabricated a thermoelectric generator consisting of sputtered polyimide stripes arranged parallel to each other that are electrically connected in a row. And in 1999 Seiko launched a watch with a built-in thermoelectric generator that uses the body heat. With the help of highly-developed micromachining technology more than 1000 thermocouples could be stacked and finally placed inside the watch.

However, being competitive in price with standard batteries, the use of low-cost-materials and low-cost-production methods is inevitable.

To simplify the production process we present a wearable thermoelectric generator consisting of one very long stripe that is coiled-up to a small spiral. Furthermore, we show that screen printing is an ideal low-cost production technology by fabricating screen printed thermocouples, First results are given.

2. The principle of coiling up

While the required power is very low for power consumers like a wrist-watch (1–10 μW), usually a relatively high voltage

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in the range of about 1 V and a low current of only some μA are needed.

This is in contrast to the most thermoelectric generators that have a high current output, but achieve only low voltages.

Eq. (1) shows the basic equation for the voltage of a thermoelectric generator (without load). It depends on the number of thermocouples n that are electrically connected in series, on the available temperature difference ΔT and on the specific thermoelectric coefficients of the used pair of materials α_1, α_2, also known as thermopower.

$$V_{\text{output}} = n\Delta T(\alpha_1 - \alpha_2) \tag{1}$$

For a generator using the temperature difference between the body heat and the surrounding air ΔT usually is not very high, perhaps only 4 or 5 K. Since $\alpha_1 - \alpha_2$ will not exceed 150 μV/K for most low-cost thermoelectric materials, it can be clearly seen that the needed voltage output can only be generated by a series connection of some thousands of thermocouples.

However, also when fulfilling the requirements in voltage and current for a special application, thermoelectric generators will only be an appropriate replacement for batteries when they do not exceed them in size and prize. Therefore, this huge amount of thermocouples has to be fabricated in low-cost-production, but nevertheless they all must be arranged at a small space.

With the principle of coiling-up we present a solution for both:

Using a very long stripe of polymer foil as substrate, many thousands of thermocouples can be easily prepared within a meander structure since there is much space. After that, the foil is coiled-up to a coin-size shape, as shown in Fig. 1. Since the foil thickness can be very thin (usually several μm), some meters of foil stripe can be coiled-up on small space of about 1 cm^2. Coiled-up, all thermocouples are automatically thermally connected in parallel, which means that each of them gets the full temperature difference between both sides of the generator.

3. Design optimization

As the generator is designed to work with the body heat versus the surrounding room temperature, it is very important to optimize the dimensions for this specific application in order to achieve a maximum power output per cm^2. For that the thermal resistance of the generator has to be adapted to that of body and clothing. In analogy to an electrical circuit the maximum power output per cm^2 will be yield when the thermal resistance of the generator (per area) equals that of the human body (per area). Although the thermal resistance of the body can vary at different skin areas, a basic estimation can be done as follows:

At a temperature difference of about 15° between air and body temperature, a normal person needs about 2000 kilo-calories per day, which is about 8400 KJ. This energy amount is completely converted into heat, which means an average heat power of about 100 W. But this value is valid for a person in air. Here the surrounding air film normally acts like an additional series resistance to the thermal resistance of the body itself. However, this additional resistance cannot be taken into account because it does not exist when bringing skin and thermogenerator into perfect contact. The idea of a person in water is a good model where the thermal body resistance can be calculated because in this case a good thermal contact is guaranteed. In water the energy loss is about 20–25 times higher as it is in air at the same temperature. This means a power of about 2–2.5 KW. Assuming a typical skin surface of about 2 m^2, this leads to an average thermal resistance (per area) of about 100 K cm^2/W just for the body.

In order to match the thermal resistance of a generator with the coiling-up-design, three dimensions are decisive: the thickness of the polymer foil, the thickness of the thermoelectrical material layers and the width of the stripe (which corresponds to the generator height). All are shown in Fig. 2. Although foil thickness should be as thin as possible in order to allow the coiling up of long stripes to a small space, the foil should have enough stability for processing. Several experiments showed that a polyimide foil with a thickness of 12.5 μm seems to be the best compromise. We decided not to change this value for thermal adaptation. Varying the layer thickness and the stripe width (=generator height) should be the better choice. Hence, there is the possibility to choose the dimension of one (e.g. the stripe width) and calculate the other (e.g. material layer thickness) in order to get the desired thermal resistance for the coiled-up generator. The

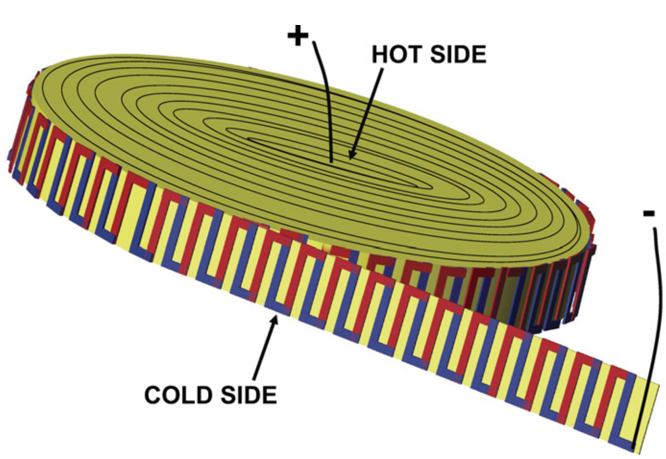

Fig. 1. Schematic of the coiled-up thermoelectric power generator.

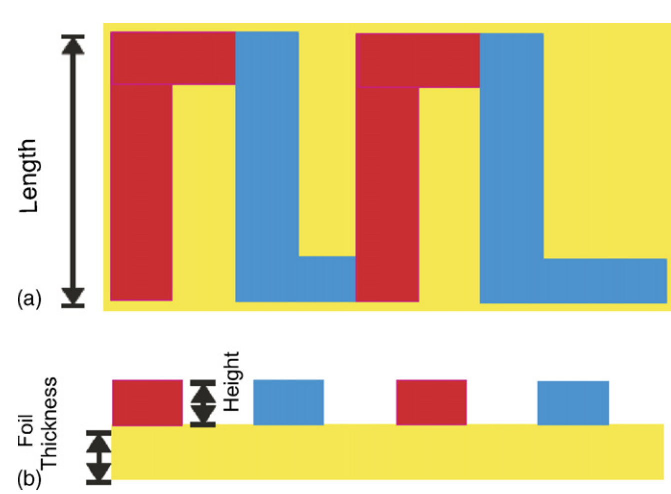

Fig. 2. (a and b) Decisive dimensions for the adaption of the thermal resistance.

low thermal conductivity of the polymer foil allows thermally perfectly adapted generators with small heights of only some millimetres. Thinking of "simple" thermoelectric materials like antimony and bismuth on a polyimide substrate, a metal thickness of 1 and 3 μm, respectively, on a 12.5 μm thick substrate with a stripe width of 10 mm result in a perfect match of the thermal resistance.

We found that the concept of coiling up thin foils indeed allows for using the combination of these simple materials. For a wrist-watch about 1 V is required. Since a battery size of about 1 cm^2 can be assumed, consuming the same space should be acceptable for the thermogenerator. When coiled-up, a stripe length of about 5 m of foil can be placed on this area. This length allows a huge series connection of thermocouples, generating quite easily the demanded voltage.

Compared to pure antimony and bismuth, complex thermoelectric materials such as Bi_2Te_3, Sb_2Te_3, or Bi_2Se_3 have a higher thermopower [6], but are much more expensive and more complicated to handle. With the principle of coiling up, they can be avoided: using antimony and bismuth with a thermopower of only 100 μV/K and assuming a temperature difference of only 4°, about 2500 pairs are necessary to realize 1 V. This large number can be placed on the 5 m-stripe without any problem. Choosing the thermocouple width to be 2 mm (which corresponds to the smallest structure size of 500 μm), a low-resolution, low-cost production technique is sufficient. Of course, even wider structures are thinkable, especially when higher currents are needed.

4. Materials and fabrication technology for the prototype

Polyimide (Kapton) was chosen as substrate because of its superior temperature resistance. Antimony and bismuth were chosen as relative cheap thermoelectric materials with satisfactory properties as explained above.

To test the principle of coiling up, a first generator was fabricated by sputtering through a shadow mask. A stripe with a length of about 1.8 m was fabricated, having 900 thermocouples on it. It can be noted that the adhesion of the antimony and bismuth on Kapton is strong enough so that the stripe can be coiled-up in a very tight radius of only some mm without blistering of both metal films.

5. Prototype: results and discussion

In awareness of the fact that thin sputtered metal films have a lower electrical conductivity than bulk material [7,8], first sputtering tests showed that the electrical conductivity of bismuth was only about 50% of the expected value.

In order to compensate this effect, the sputtered bismuth height was doubled to about 6–7 μm. With these dimensions, the whole generator stripe showed a resistance of about 75 kΩ before coiling-up. This is about six times the value of idealistic bulk-material-calculations. When the long stripe was coiled-up to a spiral, we observed no change of the generator resistance, even when the inner radius of the spiral was chosen to be only 1 mm. Also under the microscope, no changes of the metal layers (like blistering or peeling) could be observed. So we state that the adhesion of the sputtered antimony and bismuth to the kapton-foil is strong enough for coiling-up, which validates the whole concept.

To measure the achievable thermopower of the sputtered thermocouples, the thermal contact has to be as good as possible. So for first tests a short generator-stripe with only 30 thermocouples was pressed between two clamps, each consisting of a pair of metal blocks. A draw of the setup is shown in Fig. 3. To avoid electrical shortcuts, the surface of the blocks was covered with a thin insulating polymer film. While one pair of blocks was heated by a hotplate, the other pair was held at room temperature. Temperature measurements were done using a voltcraft 302 K/J Thermometer with a thermocouple-temperature-sensor. With this fast-reacting thermometer the temperature could be measured directly beneath the generator stripe, so we assume that the measurement error is not bigger than 1 K. Electrical measurements were done with a keithley "model 2001" multimeter.

For this setup with a good thermal contact to a short section of the stripe, a thermopower of 65 μV/K could be reached for one single thermocouple, compared to the value from literature [6] of about 100 μV/K. Note that we did not try to enhance this value, e.g. by thermal annealing. From these measurements, the voltage and power output per cm^2 can be calculated, as it is shown in Fig. 4. As the generator height is exactly 1 cm, the power output per cm^2 is equal to the power density (=power per volume) of the generator (in μW/cm^3). The graph clearly shows the generator optimization towards high voltages on a small base area, even at low temperatures. Using a generator with a base area of 1 cm^2 at a temperature difference of only 5 K, both typical values for the real use, more than 0.8 V can be generated. On the other side it can be seen that the power output is quite low – about 0.8 μW at 5 K temperature difference – which is a tribute to the used low-cost materials antimony and bismuth. But thinking of a generator with the size of only 2 cm^2 about 1.6 V and 1.6 μW could be produced, what is enough for a wrist-watch. For that

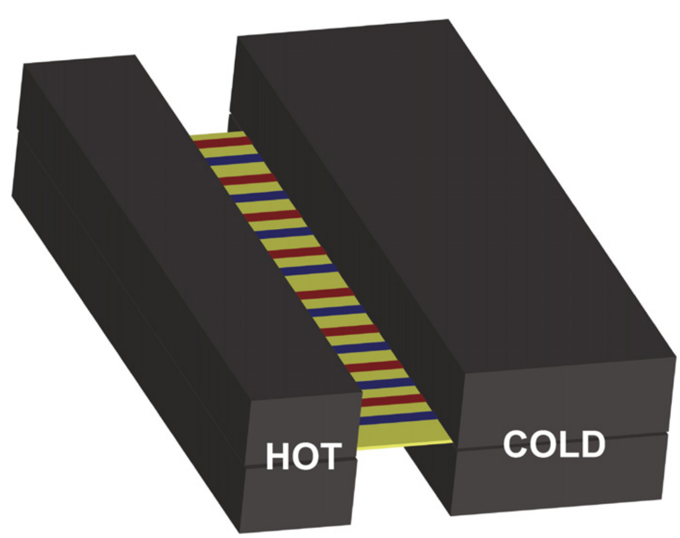

Fig. 3. Measurement setup: thermal connection to a short thermogenerator stripe.

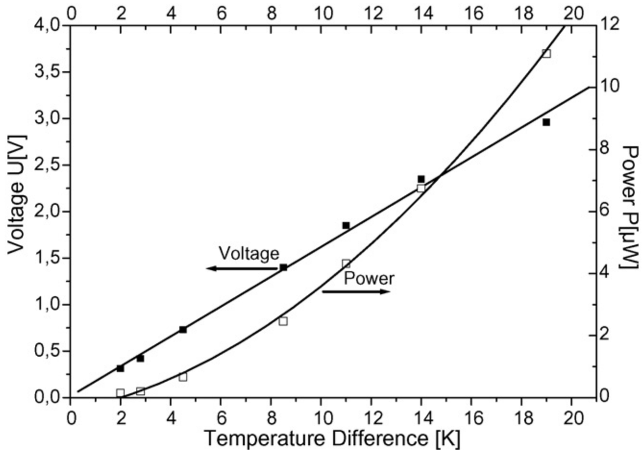

Fig. 4. Measured voltage and power (with adapted resistance)—normalized to 1 cm^2 base area.

purpose only the generator height needs to be smaller. If the height is lowered, the thermal adaptation leads to thinner and shorter metal layers. Compared to the 10 mm-thick generator, calculations showed that for a 5 mm-thick generator the power will be reduced by about 15% and for a 2.5 mm-thick-generator by about 40%. This is mainly due to enhanced heat loss through the polymer substrate. So in real applications there has to be a trade off between what height can be accepted and what power is needed. Although power densities up to about 2 $\mu W/cm^3$ at 5 K temperature difference are possible with the used low-cost materials, we think that this is not the most important fact. Especially for low-power-consumers like a wrist watch not the power-need (of about 1 μW), but the required voltage (of about 1 V) is the main challenge.

Compared to the results with the small stripe, first experiments with the coiled-up generator showed only very small voltages. This came from a poor thermal connection of the heat source and heat sink to the top and bottom side of the coiled-up spiral because of an air gap of up to 2 mm resulting of fluctuations in stripe width that are caused by hand-cutting of the stripes.

So for further measurements with the whole generator, the 1.8 m long stripe was coiled around a core consisting of two round aluminium plates (with a diameter of 35 mm) which are laid over each other with polystyrene as insulation between the two metal plates. The whole setup, including the coiled-up generator is shown in Fig. 5. With this measuring setup about 31 mV/K could be reached for the whole generator, which corresponds to 34 μV/K for each thermocouple. Compared to the measurement of a single stripe, this is only about half of the achievable thermopower. Once again a not sufficient thermal connection is the reason for this, because coiling around the core leads to a good thermal connection only for the internal layers, but not for the outer ones.

So we could show that the coiled-up generator works, but the thermal connection to the whole generator surely has to be improved in the future, for example by using machine-cutted stripes and a machine-made coiling-up and by using heat conducting paste on the top and bottom of the coil.

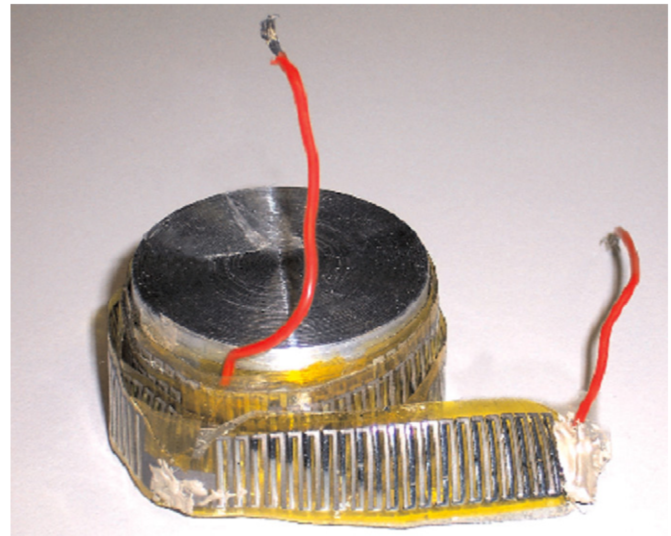

Fig. 5. Picture of the sputtered prototype.

6. Low-cost production method: screen printing

Our prototype generator, produced by means of sputtering, showed that coiling-up is an excellent principle to easily get a high amount of thermocouples in series connection.

However, sputtering or evaporation (especially through shadow masks) might be too costly for future mass market products. Since coiling-up allows a reel-to-reel production process, alternative methods might be employed to reduce production cost.

The demand for a minimal line width in the range of about 500 μm and film thicknesses of several μm do not require expensive thin film techniques. Thick film processes like screen printing seem to be more adequate. The screen printing technique promises a high product throughput. It is commonly used for printed circuit boards. For screen printing of conductive connections, a metal powder is mixed with a binder in order to get a printable metal ink. After printing the paste is heated up to evaporate the solvent in order to bring the powder particles into contact with each other which generates the electrical conduction.

Until now, only metals like silver or platinum are used in conductive inks, so no printing inks could be found using antimony or bismuth as filler.

For preparation of a self-made printing paste, antimony and bismuth powder were purchased by Goodfellow with the smallest available particle size (4 μm for antimony and 37 μm for bismuth).

As a binder tests were carried out with three different substances:

- ethylene glycol,
- commercial 2-component epoxy glue (Epo-Tec 360)
- polymethylmethacrylate (PMMA), dissolved in various amounts of 4-methyl-2-pentanone (MIBK)

The first screen prints, done with pastes with an antimony or bismuth content from 70 to 90 mass%, did not give conductive

lines, unfortunately. We conclude that there seem to be a native oxide on the surface of the antimony and bismuth particles. By chemical reduction of surface oxide using sodium borohydride we got printable pastes that led to conductive lines. Here, the ethylene glycol based pastes showed the best printability so that they were used for further experiments. Thermocouples could be printed, consisting of one leg line of antimony and one leg line made of a $Bi_{0.85}Sb_{0.15}$-alloy. This alloy was chosen because it should have a higher thermopower than pure bismuth [7].

7. Screen-printed thermocouples: results and discussion

Since a high voltage is desired, measuring the voltage generated by screen-printed thermocouples was of great interest. Fig. 6 shows the linear dependence between the temperature difference and the voltage of one single screen-printed thermocouple. The thermopower can be calculated from the slope, which leads to a value of about 97 μV/K. Although we could not reach the theoretical value of about 140 μV/K for this pair of materials, it not only validates that screen-printing is a possible production technology for thermogenerators but also shows the advantage of the $Bi_{0.85}Sb_{0.15}$-alloy compared to pure bismuth.

For a high power output also the electrical resistance of the generator is very important.

The screen printed antimony showed a specific electrical resistance of about $10^{-2}\,\Omega\,\mathrm{cm}$, while those of the printed $Bi_{0.85}Sb_{0.15}$-alloy was only in the range of $10^{-1}\,\Omega\,\mathrm{cm}$. The conductivity is 2 and 3 orders of magnitudes, respectively, lower than that of the bulk material. Of course, it is generally known that screen printed structures have higher resistances than the bulk material since the powder inside the paste is not molten so that the current has to "find its way through the particles". But since these were the first results, there is a lot of optimization that still can be done: By finding the ideal particle size, optimizing the reduction of the native surface oxide, looking for the best ratio of metal powder and screen-printing binder and searching for the best annealing temperature, it should be possible not only to drastically improve the conductivity of the screen-printed layers, but also enhance the thermopower from the achieved 97 μV/K closer to the theoretical value of about 140 μV/K.

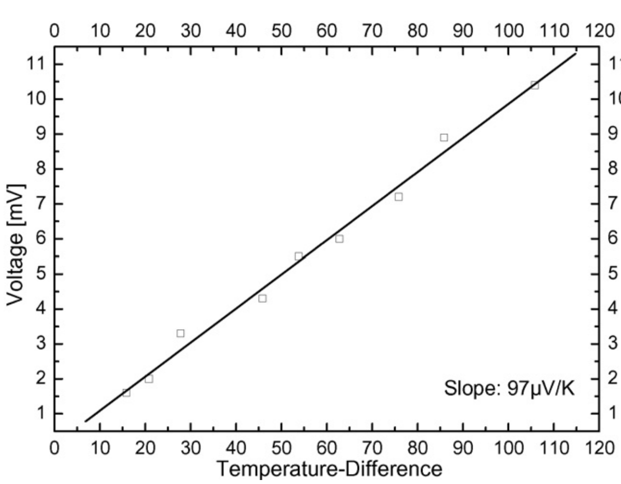

Fig. 6. Measured voltage for a screen-printed thermocouple.

8. Conclusion and outlook

Thermoelectric power generators that use body heat as energy source are well appropriate for power supply of low-energy-consumers. In order to be competitive on the market, they must be small and cheap, like a battery. The usage of polymer foil as a substrate and the principle of coiling-up helps to achieve high voltages on a small generator area with a simple technique, even when using more simple, more low-cost materials than in common thermogenerators. The validation of this idea could be given by presenting a generator prototype, fabricated by sputtering.

Since the smallest structures need not to be smaller than some 100 μm and layer thicknesses are in the range of some microns, the use of fast low-cost-production methods like screen-printing is possible. Screen-printing pastes of antimony and of $Bi_{0.85}Sb_{0.15}$-alloy were developed and the printed thermocouples obtained showed a good thermopower with an acceptable electrical resistance.

Our future work is focused on the further improvement of the screen-printing pastes. Both printability and electrical conductivity should be enhanced. Also thermal conductivity measurements of the printed structures need to be done, since with the screen-printing technology a low-cost-thermoelectric generator, not bigger than a watch battery and well suitable for wearable electronics like a wrist-watch or a hearing aid, should be within reach.

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Biographies

Jochen Weber studied electrical engineering at the Technical University of Ilmenau, Germany, where he recieved his diploma degree in 2005. Since then he is working at the IMM Institut für Mikrotechnik Mainz on the field of polymer

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Karin Potje-Kamloth received her PhD degree in physical chemistry at Ludwigs-Maximilians-Universität München. Currently, she is a senior scientist at Institut fuer Mikrotechnik Mainz GmbH. Her research interest comprises the development and fabrication of polymer hybrid systems as well as theory and applications of organic semiconductors and electroactive polymers, particularly in the field of organic electronics, low cost chemical sensors, energy harvesting, intelligent packaging smart and engineering of nanofunctionalized polymers.

Frank Haase received his diploma degree in electrical engineering at the Technical University of Ilmenau, Germany, in 2003. After 1 year as a research assistant and PhD-student at TU Ilmenau he joined the IMM Institut für Mikrotechnik Mainz. As a PhD student he is working there on the field of electron optical microsystems.

Peter Detemple born in 1950, received a diploma and a PhD in experimental nuclear and particle physics at the University of Bonn where he took a position as a scientific fellow at the electron accelerator facilities of the Physical Institute. In June 1991 he joined IMM and became leader of the plasma technology group in 1992. Research work was focused on applications of plasma-assisted surface modification processes and on applications of microtechnology in medical and bio-diagnostic devices. Since 2002, Peter Detemple is head of IMM's Microstructuring Technology Department which includes units for research and development in the fields of nanosystems, 3D-MST-applications and Laser micromachining.

Friedemann Völklein obtained both his BSc and DSC degrees in physics from University of Jena. He is professor of engineering physics at the University of Applied Sciences Wiesbaden, Germany. His main areas of interest are solid-state physics of thin films, their application in thermoelectric sensors, but are also in the field of structuring and patterning of glass.

Theodor Doll received his diploma in physics at Munich University 1988 and his PhD in Electrical Engineering in 1995 at the Bundeswehr Universität Munich. After his post doctoral stay at Universidad de Chile, Santiago 1996 he was assistant professor in Micro Systems 1997 in Munich and 1998 visiting associate at Caltech. In 2000 he was appointed a full professorate in solid state electronics at Ilmenau Technical University, Germany and 2002 director of the Center of Micro- and Nanotechnologies, ZMN there. Since 2004 he is managing scientific director and professor of microstructure physics at the IMM Institut für Mikrotechnik Mainz and University of Mainz, respectively, Germany. His research interests are micro- and nanotechnology with focuses in chemical sensing, polymer systems, nano optics and 3D micro structures.